THE
FUNDAMENTALS
OF
ELECTROCHEMISTRY
AND
ELECTRODEPOSITION

by

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published under the auspices of the AMERICAN ELECTROPLATERS' SOCIETY

1960

FRANKLIN

PUBLISHING COMPANY, INC. *palisad , n w jersey*

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CHAPTER I

THE FORMATION OF SIMPLE IONS

Importance of Ions

IF we were asked to explain in the simplest terms the processes of electroplating or electrodeposition, we should say that they consist in the passage of an electric current through a solution and the separation of a metal on one of the electrodes. Both of these fundamental processes depend on the existence in the solution of charged particles known as "ions." An ion is an atom or group of atoms that has acquired an electric charge; this charge may be positive or negative in sign. These ions carry the current through the solution, and when they give up their charges at the electrodes, the resulting uncharged material will, in certain circumstances, form a "deposit" or "plate." It is clearly important for us to try to understand something about the nature and properties of ions.

According to modern views, every atom consists of a small nucleus carrying a net positive charge surrounded by a number of negatively charged particles, known as "electrons." The number of electrons around the nucleus of any atom in its normal or neutral state is equal to the positive charge on the nucleus. The resultant charge of the atom as a whole is, therefore, zero. The nuclear charge, and hence the number of electrons surrounding the nucleus, increases steadily with increasing weight of the atom. For example, the nucleus of the atom of hydrogen, the lightest known atom, carries a single positive charge and there is a single electron moving around it. The next heaviest elements in order are helium, lithium, beryllium, boron, carbon, etc., and their nuclei carry two, three, four, five, six, etc., charges, which are surrounded by the same number of electrons, respectively. The nuclear charge and the number of electrons increases steadily until with uranium, the heaviest element, there are 92 electrons around the nucleus. The number of positive charges on the nucleus, and hence the number of electrons in the atom is referred to as the "atomic number."

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CHAPTER III

Ions in Solutions of Electrolytes

Electrolytic and Metallic Conductors

SOLUTIONS of strong acids, such as hydrochloric and sulfuric acids, of strong bases, such as sodium and potassium hydroxides, and of many salts in water are able to conduct the electric current efficiently. Such conducting solutions are generally known as "electrolytic" conductors, or briefly, as "electrolytes." They differ from metallic conductors in an important respect. The passage of an electric current through a solution is always accompanied by a transfer of matter; this becomes evident at the plates, or "electrodes," used for conveying the current into and out of the solution. With a metallic conductor there is no such movement of matter, and even if two or more different metals are joined, no change can be observed at the junction between them. On the other hand some form of chemical action, such as the plating out of a metal or gas or a metal dissolving, is always observed at the junction between a metallic conductor and an electrolytic solution.

Ions in Electrolytes

The difference in behavior between metals and electrolytes when conducting an electric current is due to the fact that in a metal the current is carried by electrons only, and there is no movement of particles associated with mattter. In electrolytes the current is carried by positive and negative ions which, as seen in the previous chapters, consist of atoms or groups of atoms that have acquired special stability by losing or gaining one or more electrons. Since these ions are material particles, made up of various elements, the flow of the electric current, which is accompanied by the movement of these particles, must be associated with the transfer of matter.

CHAPTER XVIII

CONDITIONS AFFECTING THE FORM OF ELECTRODEPOSITED METALS

Factors Affecting Nature of Deposit

IT was seen in the previous chapter that good deposits of metallic silver can be obtained from cyanide solutions, but that such deposits are not obtainable from solutions of silver nitrate. There are numerous instances in connection with electrodeposition in which the conditions of plating make a considerable difference in the physical appearance and other properties, such as hardness, of the deposit. It is, therefore, a matter of fundamental importance to try to understand how the nature of the plate is affected by the conditions of electrolysis. The whole problem is undoubtedly very complex, but there are certain generalizations which can be made that provide at least a partial solution. Electrodeposited metals are undoubtedly crystalline in nature, and the form of the deposit depends largely on two factors; first, the rate of formation of crystal nuclei by the discharge of the ions at the cathode, and second, the rate at which these nuclei grow into large crystals. If the conditions are such as to favor the rapid formation of fresh nuclei on the cathode, the deposit will tend to consist of small, fine-grained crystals. The plate will then be smooth and relatively hard; this is the case in the ordinary plating of silver, nickel, chromium, and so on. On the other hand, if the circumstances are such that the nuclei increase in size rapidly, the deposit will consist of relatively large crystals and will be rough in appearance. The separation of silver from silver nitrate solution evidently takes place under such conditions. Sometimes electrodeposits are spongy or powdery in character: the crystals are then small, but the presence of an impurity probably prevents them from adhering to form a continuous plate.

There are undoubtedly many factors, not all clearly understood, that

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influence the two processes referred to above, namely, formation of crystal nuclei and their increase of size, but five at least may be considered. These are (1) current density (C.D.), (2) concentration of the electrolyte, (3) temperature, (4) presence of addition agents, and (5) nature of the electrolyte. These factors will be considered in turn.

Current Density

At low C. D.'s the discharge of ions occurs at a slow rate; there is thus ample time for the crystal nuclei to grow, and the formation of fresh nuclei is unnecessary. The deposits obtained under these conditions should be coarsely crystalline. As the C. D. is increased, the rate of discharge of the ions will increase and fresh nuclei will tend to form; the plate will then consist of smaller crystals. Increase of C. D., within limits, will therefore yield deposits that are more fine-grained. There is, however, a definite limit to this improvement, because at very high C. D.'s the crystals tend to grow out from the cathode toward regions where the solution is more concentrated; in this way "trees" or nodules are obtained. Further, at high C. D.'s there may be considerable discharge of hydrogen ions, thus causing the solution in the cathode layer to become alkaline and precipitate hydroxides or basic salts. The inclusion of appreciable amounts of these substances in the deposit may make the latter fine-grained (see below), but it will be dark in color, i.e., "burnt", or spongy in character. Further, the evolution of hydrogen gas is often accompanied by the formation of spots and streaks on the plate.

Concentration of the Electrolyte

Increase of concentration can largely offset the bad effects of high C. D.'s. By increasing the concentration of the solution, or by the use of agitation, it is possible to postpone until much higher currents the harmful effects, such as tree formation, and burnt or spongy deposits, accompanying the use of high C. D.'s. Since in commercial electroplating it is desirable for the sake of economy to work at the highest practicable C. D.'s, the bath solution should be as concentrated as is reasonable and some form of agitation or stirring should be employed. Under these conditions, the solution near the cathode does not become impoverished in the ions to be discharged (see Chapter XVI), and there is little tendency to form trees, dark deposits, etc. Some electrochemists have expressed

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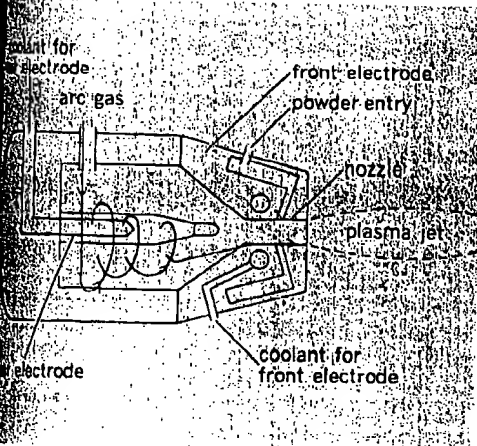

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Fig. 3. Cross-sectional diagram of plasma-spray jet.

Sprayed refractory coatings have been developed for high temperatures experienced in aerospace applications. They are also used for wear resistance, heat resistance, and electrical insulation.

Cementation coatings. These are surface alloys formed by diffusion of the coating metal into the base metal, producing little dimensional change. Parts are heated in contact with powdered coating material that diffuses into the surface to form an alloy coating, whose thickness depends on the time and the temperature of treatment. A zinc alloy coating of 0.001 in. (25 μm) is formed on steel in 2–3 hr at 375°C (700°F). A chromium alloy (chromized) coating of 0.004 in. (100 μm) is formed in 1 hr at 1000°C (1830°F).

Chromized coatings on steel protect aircraft parts and combustion equipment. Sherardized (zinc-iron alloy) coatings are used in threaded parts and castings. Calorized (aluminum-iron alloy) coatings protect chemical equipment and furnace parts. Diffusion coatings are used to provide oxidation resistance to refractory metals, such as molybdenum and tungsten, in aerospace applications where reentry temperatures may exceed 3000°F (1650°C). In addition to the pack process described above, such coatings may be applied in a fluidized bed. In forming disilicide coatings on molybdenum, the bed consists of silicon particles suspended in a stream of heated argon flowing at 0.5 ft/sec (0.15 m/s), to which a small amount of iodine is added. The hot gases react with the silicon to form SiI$_4$, which in turn reacts with the molybdenum to form MoSi$_2$.

Vapor deposition. A thin specular coating is formed on metals, plastics, paper, glass, and even fabrics. Coatings form by condensation of metal vapor originating from molten metal, from high-voltage (500–2000 volts) discharge between electrodes (cathode sputtering), or from chemical means such as hydrogen reduction or thermal decomposition (gas plating) of metal halides. Vacuums up to 10⁻⁶ mm mercury (10⁻⁴ Pa) often are required.

Aluminum coatings of 0.000005 in. (0.125 μm) are formed on zinc, steel, costume jewelry, plastics, and optical reflectors. Chemical methods are capable of forming relatively thick coatings, up to

0.010 in. (250 μm). The 200-in. (5-m) mirror for the Mount Palomar telescope was prepared by vapor coating with aluminum in a vacuum chamber 19 ft (5.8 m) in diameter and 7 ft (2.1 m) high.

Immersion coatings. Either by direct chemical displacement or for thicker coatings by chemical reduction (electroless coating), metal ions plate out of solution onto the workpiece.

Tin coatings are displaced onto brass and steel notions and on aluminum-alloy pistons as an aid during the breaking-in period. Displacement nickel coatings of 0.00005 in. (1.25 μm) are formed on steel articles. Electroless nickel, involving the reduction of a nickel salt to metallic nickel (actually a nickel-phosphorus alloy), permits the formation of relatively thick uniform coatings up to 0.010 in. (250 μm) on parts with recessed or hidden surfaces difficult to reach by electroplating.

Vitreous enamel coatings. Glassy but noncrystalline coatings for attractive durable service in chemical, atmospheric, or moderately high-temperature environments are provided by enamel or porcelain coating. In wet enameling a slip is prepared of a water suspension of crushed glass (see FRIT), flux, suspending agent, refractory compound, and coloring agents or opacifiers. The slip is applied by dipping or flow coating; it is then fired at a temperature at which it fuses into a continuous vitreous coating. For multiple coats the first or ground coat contains an oxide of cobalt, nickel, or molybdenum to promote adherence.

Dry enameling is used for castings, such as bathtubs. The casting is heated to a high temperature, and then dry enamel powder is sprinkled over the surface, where it fuses.

Firing temperatures for conventional enameling of iron or steel ranges up to 870°C (1600°F). Low-temperature enamels have been developed, permitting the enameling of aluminum and magnesium.

Coatings of 0.003–0.020 in. (75–500 μm) are used for kitchenware, bathroom fixtures, highway signs, and water heaters. Vitreous coatings with crystalline refractory additives can protect stainless steel equipment at temperatures up to 950°C (1740°F).

Ceramic coatings. Essentially crystalline, ceramic coatings are used for high-temperature protection above 1100°C (2000°F). The coatings may be formed by spraying refractory materials such as aluminum oxide or zirconium oxide, or by the cementation processes for coatings of intermetallic compounds such as molybdenum disilicide. Cermets are intimate mixtures of ceramic and metal, such as zirconium boride particles, dispersed throughout an electroplated coating of chromium. See CERMET.

Surface-conversion coatings. An insulating barrier of low solubility is formed on steel, zinc, aluminum, or magnesium without electric current. The article to be coated is either immersed in or sprayed with an aqueous solution, which converts the surface into a phosphate, an oxide, or a chromate. Modern solutions react so rapidly that sheet and strip materials can be treated on continuous lines.

Phosphate coatings, equivalent to 100–400 mg/ft² (1–4 g/m²), are applied to bare or galvanized steel and to zinc-base die castings as preparation for painting. The coating enhances paint adhesion